JOURNAL OF CURRENT RESEARCH IN SCIENCE (ISSN 2322-5009)
CODEN (USA): JCRSDJ
2013, Vol. 1, No. 6, pp:440-443
Available at www.jcrs010.com

ORIGINAL ARTICLE

PREDICTION OF METHIMAZOLE SOLUBILITY IN SUPERCRITICAL CARBON DIOXIDE: EFFECTS OF EQUATIONS OF STATE AND MIXING RULES

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ABSTRACT: Predictions of the solubilities of industrial solid compounds in supercritical carbon dioxide have been a challenge in recent years. In this work, evaluation of the solubilities of Methimazole in the supercritical carbon dioxide was predicted by the Peng–Robinson (PR) and the soave-Redlich-kwong with two mixing rules including the Wong–Sandler (WS) and the van der Waals (VDW). The results indicate that, the combination of the PR EOS with the WS mixing rule leads to better correlation (AAD=7.14%) compared with other ones.

KEYWORDS: Thermodynamic modeling, Supercritical carbon dioxide, Solid solubility, Equation of state.

INTRODUCTION

There has been a considerable increasing interest in using supercritical fluids (SCFs) as an alternative solvent in many industrial applications, such as in chemical and biochemical reactions, extraction and purification processes, particle production or more recently in materials and polymer processing (JafariNejad *et al.*, 2010). Supercritical fluids are attractive solvents for different applications because of their unique properties, particularly the ability to adjust the solvent strength by changing the temperature or pressure. Because of carbon dioxide's unique properties like relative low critical temperature and pressure, this compound has found many new applications (Mehdizadeh *et al.*, 2011). In order to design and develop supercritical processes, it is necessary to obtain solubility data of the considered compounds. Unfortunately, the experimental measurements are often difficult, time-consuming and costly (Stefani *et al.*, 2004; Yazdizadeh *et al.*, 2011). Thus, it is desirable to develop estimation methods for correlating and predicting solubility data at various pressures and temperatures. There are three main models for this aim: equations of state, empirical, and cluster solvation models (Stefani *et al.*, 2004). To predict the solubility of a solute in supercritical fluids, Equation of State (EOS) models are widely used. Cubic EOS's are the simplest equations capable of predicting and estimation fluid phase equilibrium. In this work, we evaluate the effect of two equations of state including the SRK and the PR and two mixing rules along with the Wong–Sandler (WS) and the van der Waals (VDW) on prediction of the solubility of Methimazolein supercritical carbon dioxide. The optimal values of the model adjustable parameters are exhibited using experimental data points.

THERMODYNAMIC MODELING

EOS approach, the supercritical fluid is assumed as high-pressure gas, while inother approaches, the supercritical fluid are treated as a liquid. The solubility of a solid (component i) in supercritical carbon dioxide (component j) can be predicted as:

$$y_2 = \frac{P_2^s \varphi_2^s e^{v_2^s (P - P^{sat})}}{\varphi_2 P} \quad (1)$$

Where, P_2^s is the sublimation pressureof the solid, φ_2^s is fugacity coefficient of thesolid in the sublimation pressure usually equal to one, v_2^s is the solid molar volume and φ_2 is the fugacity coefficient of the solid in the supercritical phase, which can be derived from any EOS by following the well-known thermodynamic relationship:

$$RT \ln \varphi_2 = -RT \ln Z + \int_V^\infty \left\{ \left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_{i \neq} n_j} - RT/V \right\} dV \quad (2)$$

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In order to calculate the fugacity, PR and SRK equation of state were used. PR equation is as follows:

$$P = \frac{RT}{v-b} - \frac{a}{v^2+2bv-b^2} \quad (3)$$

Where a and b are the attraction and repulsion parameters for pure substances. For PR EOS these parameters can be calculated by the following equations:

$$a = \frac{0.45724 R^2 T_C^{2.5}}{P_C}\left(1+\left(1-\frac{\sqrt{T}}{T_C}\right)\times(0.37464+1.54226\omega-0.26992\omega^2)\right)^2 \quad (4)$$

$$b = \frac{0.778 R T_C}{P_C} \quad (5)$$

SRK equation of state is as follows:

$$P = \frac{RT}{v-b} - \frac{a}{v^2+bv} \quad (6)$$

$$a = \frac{0.427447 R^2 T_C^2}{P_C}\left(1+\left(1-\sqrt{T_r}\right)\times(0.48+1.574\omega-0.176\omega^2)\right)^2 \quad (7)$$

$$b = \frac{0.08664 R T_C}{P_C} \quad (8)$$

In these equations, ω is acentric factor and T_c and P_c are critical temperature and pressure of each component. In order to calculate the mixture parameter (a and b) in EOS approach, the mixing and combining rules were used for the EOS parameters. Table1 summarizes the mixing and combining rules used in this work. In WS mixing rule, C is an EOS-dependent constant (VdW: C=-1, SRK: C=-ln2, PR: C=-0.623) and the single adjustable parameter (kij) for each binary pair is referred to as the WS mixing rule parameter (k12) (Zanganeh *et al.*, 2011). In this paper, the excess Gibbs energy (G^E) is calculated According to Van-Laar activity model as the equations below:

$$\frac{G^E}{RT} = \frac{A_{12}A_{21}y_1y_2}{A_{12}y_1+A_{21}y_2} \quad (9)$$

$$\ln\gamma_1 = A_{12}\left(1+\frac{A_{12}y_1}{A_{21}y_2}\right)^{-2}, \ln\gamma_2 = A_{21}\left(1+\frac{A_{21}y_2}{A_{12}y_1}\right)^{-2} \quad (10)$$

The interaction parameters of each model are obtained by fitting experimental data, through the minimization of an objective function, the average absolute relative deviation (AARD), defined by the equation (11) (Sridara et al., 2013).

$$AARD(\%) = \frac{100}{N}\sum_{i=1}^{N}\frac{|y_{i,calc}-y_{i,exp}|}{y_{i,exp}} \quad (11)$$

In this equation, N is the number of experimental data points, $Y_{i,calc}$ is the calculated solubility, and $Y_{i,exp}$ is the experimental solubility data points.

RESULT AND DISCUSSION

The physicochemical and critical properties of the Methimazole and carbon dioxide are given in Table 2 (Housaindokht *et al.*, 2008). Calculated mole fractions of Methimazole in CO_2 were compared with the experimental data (Yamini *et al.*, 2003), and values of the average absolute deviation percent (AAD%) are listed in Tables 3. Moreover, Table 4 shows the typical optimal values of the model parameters for the PR and SRK EOS. Figures 1-3 depict the comparison between experimental data and predicted results including two EOS (PR and SRK) and two mixing rules (vdW and WS) for Methimazole/CO_2 system. The results demonstrate that the PR-WS model is more accurate and reliable compared with other ones. The result of SRK-WS model is very close to PR-WS model for different ranges of temperature, but about SRK-vdW and PR-vdw, SRK-vdW is less accurate than PR-vdW.

Table 1: Summary of the cubic EOS, mixing and combining rules used in this work (Mukhopadhyay *et al.*, 2003; Wong *et al.*, 1992)

VdW	WS
$a_m = \sum_1\sum_2 y_1y_2a_{12}$, $a_{12} = \sqrt{a_1a_2}(1-k_{ij})$	$a_m = Q\frac{Q}{(1-D)}$, $b_m = \frac{Q}{(1-D)}$
$b_m = \sum_1\sum_2 y_1y_2b_{12}$, $b_{12} = (b_1+b_{2)/2}$	$Q = \sum_1\sum_2 y_1y_2\left(b-\frac{a}{RT}\right)_{12}$,
	$D = \sum_1 y_1\frac{a_1}{b_1RT} + \frac{G^E}{CRT}$,
	$\left(b-\frac{a}{RT}\right)_{12} = \frac{\left(b_1-\frac{a_1}{RT}\right)+\left(b_2-\frac{a_2}{RT}\right)}{2}(1-K_{12})$

Table 2: Physicochemical and critical properties of the Methimazole and CO_2

Substance	Tc (K)	Pc (bar)	W	Vm (ml/mol)	Sublimation vapor (bar)		
Methimazole	731.7	60.75	0.442	162.1	7.9E-5 (308K)	1.8E-4 (318K)	3.9E-4 (328)
CO2	304.18	73.7	0.239	-	-	-	-

Table 3: Absolute average deviations of the presented model results from the experimental data

Compund	T(K)	EOS	VDW1	WS	Number of data
			AARD%	AARD%	
Methimazole	308	PR	15.7501	6.0007	8
		SRK	19.1017	6.7475	8
	318	PR	31.0559	7.58	8
		SRK	33.7778	7.41	8
	328	PR	46.2373	7.4223	8
		SRK	47.9512	7.5179	8
	total	PR	44.8046	13.4585	24
		SRK	46.4829	14.7070	24

Table 4: Optimized parameter for the modeling of Methimazole solubility in CO2 with the PR/SRK-EOS and vdW/WS mixing rules

SUBSTANCE	T(K)	EOS	VDW1	WS		
			kij	kij	Aij	Aji
Methimazole	308	PR	0.3860	0.7636	0.3900	9.7963
		SRK	0.3673	0.7732	-0.0252	8.5764
	318	PR	0.4247	0.8715	-0.0070	7.0825
		SRK	0.4250	0.8594	-0.0049	6.3040
	328	PR	0.4754	0.8834	-0.0279	7.6304
		SRK	0.4694	0.8736	-0.0383	7.1721
	total	PR	0.4297	0.8870	-0.0064	6.7516
		SRK	0.4225	0.8791	-0.0046	5.3369

Table 5: average of AAD% for three temperatures

EOS/mixing rule	vdW	WS
PR	31.01%	7.14%
SRK	33.61%	7.22%

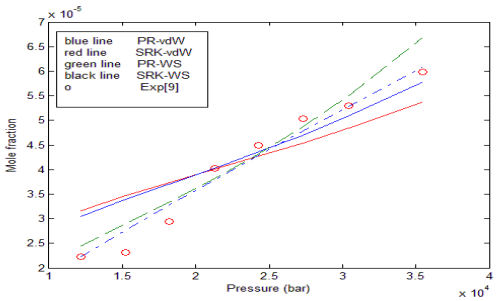

Figure 1: Solubility of Methimazole in $scCO_2$ at T=308K and comparison between experimental dataand predicted results of this work.

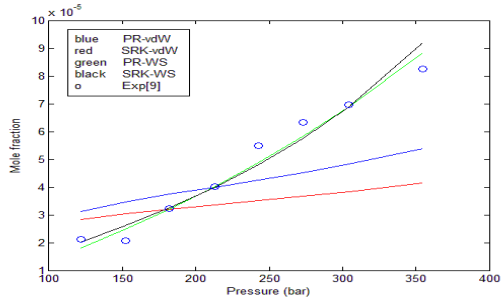

Figure 2: Solubility of Methimazole in $scCO_2$ at T=318K and comparison between experimental data and predicted results of this work.

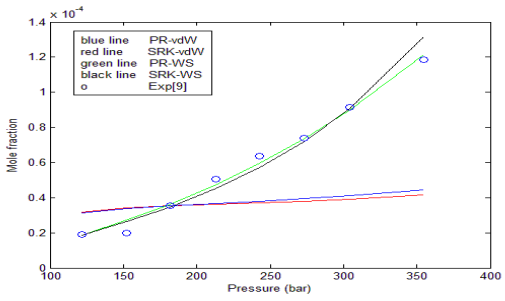

Figure 3: Solubility of Methimazole in $scCO_2$ at T=328 and comparison between experimental dataand predicted results of this work.

CONCLUSION

In this study, a thermodynamic model based on cubic equations of state (the PR and the SRK) and two mixing rules (VDW1, WS) was presented in order to calculate the solubility of Methimazole in supercritical carbon dioxide. The optimal values of the parameters of two mixing rules were calculated for two EOS model and reported in this work .It was observed that the combination of the PR-EOS and WS mixing rule leads to less average absolute deviations (7.14%) for Methimazole compared with other combinations.

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